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(54) IMPROVEMENTS IN AND RELATING TO THE MANUFACTURE OF HEAT-RESISTANT MATERIALS

(71) We, INSTITUT VYSOKIKH TEMPERATUR AKADAMII NAUK SSSR, Korovinskoe shosse, Moscow, USSR, a corporation organised and existing under the Laws of the Union of Soviet Socialist Republics, do hereby declare the invention for which we pray that a patent may be granted us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to heat-resistant porous materials.

According to the present invention there is provided a heat-resistant porous material, comprising 50—75 volume per cent of microspheres of a high-melting point oxide having a melting point in excess of 1700°C, the microspheres being 10—200 mμ in diameter and being sintered directly to each other so that the diameter of the circle of contact between the microspheres is 0.2—0.5 of the microsphere diameter.

The sintering of spherical particles results in the formation of a neck between them, and the 'circle of contact' refers to the circumference of the narrowest part of this neck.

Materials in accordance with the present invention can be used in high-temperature engineering, preferably for thermally stressed elements of power and process apparatus operating in an oxidizing atmosphere for 10³—10⁴ hours with a surface temperature of up to 2000°C. Moreover, the materials can be used for short periods at surface temperatures in excess of 2000°C, with a density of heat flux on the elements of about 17 Cal/m².hr.

Materials in accordance with the invention and manufactured from microspheres of stabilized zirconium dioxide 30—40 mμ in diameter with a contact diameter of 0.3 of the microsphere diameter and a 30% porosity, showed a compression strength of 6000 kg/cm², a tensile strength of 500 kg/cm², and an elongation of 1% at room temperature. This is a 5—10-fold increase compared with the corresponding characteristics of hitherto

proposed granular materials of a similar composition.

Materials made from aluminium oxide microspheres, 30—40 mμ in diameter, with a contact circle diameter between the microspheres of 12—15 mμ and a 35% porosity showed a compression strength of 9000 kg/cm², a tensile strength of 950 kg/cm², and an elongation of 0.7%. These values exceed by 7—10 times the corresponding characteristics of hitherto proposed porous materials. The recrystallisation velocity of materials in accordance with the invention is expressed as an alteration in grain (microsphere) geometry and size, it is substantially lower than that of hitherto proposed materials. Thus, a material made from sintered aluminium oxide microspheres 60—70 mμ in diameter did not display secondary recrystallisation upon isothermal storage for 50 hours at a temperature of 1860°C. Heat-resistant materials made from microspheres within the above size and contact range had higher strengths, deformabilities and recrystallisation resistances than hitherto proposed materials.

Materials in accordance with the invention preferably include a filler.

Due to the strength of porous material in accordance with the invention, it is possible to obtain various kinds of special purpose materials for diversified applications, such as in high-strength heat-resistant electrical engineering, and heat-insulating and thermostable materials, ensuring stable operation of various structures without changes in geometry.

For producing high-strength heat-resistant electrical engineering materials, metals, alloys, or intermetallic compounds can be used as a filler.

For manufacturing high-strength, heat-resistant, ablation materials it is preferable to use an organic compound, for example a phenol - formaldehyde resin, a polyvinyl alcohol, an epoxy resin, or an organosilicone polymer, as a filler.

Heat-resistant, high-strength, structurally-

thermostable materials can be produced using glass as a filler.

Thus, a heat-resistant structural material made from microspheres of zirconium dioxide stabilized by 6 weight per cent of calcium oxide, 92—100 $m\mu$ in diameter, with a contact diameter between the sintered microspheres of 30—40 $m\mu$ and a 35% porosity, had a compression strength of 800 kg/cm². A structural electrical engineering material of a similar composition and structure, incorporating an additional 30 volume per cent of bismuth, had a compression strength of 2100 kg/cm², and it was capable of conducting an electric current having a density of up to 100 A/cm² at a voltage of up to 50 V when operating under arc discharge conditions.

A structural ablation material made from 60 volume per cent of microspheres of zirconium dioxide stabilized by 15 weight per cent of yttrium oxide; 150 $m\mu$ in diameter, with a contact diameter between the sintered microspheres of 40—45 $m\mu$, and including 35 volume per cent of an organo-silicone polymer as a filler, was operated without changes in geometry in contact with a combustion product flow, owing to evaporation of the polymer.

A structural heat-resistant thermostable material, made from 66 volume per cent of microspheres of zirconium dioxide stabilized by calcium oxide, 92—100 $m\mu$ in diameter, with a contact diameter between the microspheres of 34—38 $m\mu$, including 25—30 volume per cent of glass with a thermal expansion coefficient of $1-3 \times 10^{-6} \text{ deg}^{-1}$, and shaped as a plate 17 mm thick, was capable of withstanding one-sided heating at a rate of up to 2—2.5 C deg/s without cracking. This was 5—6 times greater than the permissible heating rate of a plate similar in size but produced from a hitherto proposed granular material of similar composition and 18% porosity.

Materials in accordance with the invention can be made from compact, porous or hollow microspheres with a monocrystalline, polycrystalline or amorphous structure, produced from high-melting point oxides with a melting point of at least 1700°C. Stabilized zirconium dioxide, yttrium, aluminium, magnesium, hafnium, thorium, beryllium or silicon oxides can be used for the purpose. The microspheres can be produced by known methods, e.g. by plasma processing of powdered, high-melting point oxides in a high-frequency discharge, or by spraying a melt of the high-melting point oxides. The procedures can be adapted for manufacturing microspheres of diverse composition and structure, for example ranging in diameter from 10 to 500 $m\mu$. Bonding of the microspheres into a material can be effected by sintering. Thus materials made from microspheres of zirconium dioxide

can be sintered in an oxygen-gas-fired furnace at a temperature of up to 2200°C with isothermal holding for 5 hours. Materials made from microspheres of aluminium oxide can be produced by sintering at a temperature of up to 1950°C, their holding times being up to 10 hours.

Microspheres of high-melting point oxides sintered directly to each other in a certain manner should exhibit not only high recrystallization resistance and improved deformability but substantially higher strengths compared with hitherto proposed materials. The relationship between the strength of such a material and its structural elements can be expressed as follows:

$$\delta_h = \delta_0 \frac{k(1-P)^{5/3}}{\gamma \cdot h^2} \quad (1)$$

where

δ_h is the tensile strength of a porous material sintered from microspheres;

δ_0 is the tensile strength of a material in the microsphere contact zone (or the tensile strength of a compact material);

P is the volume porosity ratio (the free volume between the microspheres);

γ is the stress concentration coefficient in the microsphere contact zone

$$(\gamma = 1 + 2\sqrt{h(n-1)});$$

n is the microsphere radius/microsphere contact radius ratio

$$(h = \frac{R}{X});$$

and

k is a coefficient determined by the number of contacts between the microspheres (with the number of contacts equal to 8, k is approximately 3).

This relationship can be used to demonstrate graphically the interdependence between the strength of a porous material and its structure. It should be noted that P (volume porosity ratio) and n are preferably the controlled parameters, the " n " parameter being the main parameter in the theory of sintering. Sintering may proceed by various mechanisms. Generally, the kinetics of this process obey the following relationship:

$$\left(\frac{X}{R}\right)^\alpha = A_i R^{-\beta} \quad (2)$$

where

$\alpha=2$; $\beta=1$ in the case of viscous flow;
 $\alpha=5$; $\beta=3$ for volume diffusion;
 $\alpha=7$; $\beta=4$ for surface diffusion; and

A_i is a function of the surface energy, viscosity and diffusion coefficients. By substituting (2) in (1), and by making corresponding transformations, the following relationship can be obtained

$$\delta_n = B_i \delta_0 R^{-m} \quad (3)$$

where

B_i is a function including A_i ;

R is a microsphere radius; and

m is a coefficient (in the case of viscous flow $m=1$; for volume diffusion $m=6/5$; for surface diffusion $m=8/7$ and for evaporation or condensation $m=4/3$).

An experimental check of the above relationship has verified its validity and has determined the range of controlled parameters enabling the volume ratio of the microspheres, their size, and the contact value between sintered microspheres to be selected to be an optimum.

Microspheres of the high-melting point oxides should have diameters of from 10 to 200 $m\mu$, and should be sintered directly to each other so that their contact diameters are 0.2—0.5 of the microsphere diameters. Moreover, 50—75 volume per cent of said sintered microspheres are required in the material.

Materials in accordance with the invention are porous since 50—25 volume per cent of the materials are open air pores. The air pores can be partly filled by the filler, as will be discussed hereinafter in detail.

The above prerequisites, if fulfilled, would provide heat-resistant, porous materials with good strength, deformability and recrystallization resistance. Strengths and deformabilities 5 to 10 times those of hitherto proposed materials along with a 10—20-fold reduction in recrystallization velocity can be achieved. Such materials can be used in high-temperature engineering, especially in thermally-stressed elements of power and process apparatus operating for 10^3 — 10^4 hours in oxidizing atmospheres at surface temperatures of up to 2000°C. These elements can include, for example, electrodes and insulators of magnetohydrodynamic generators, gas turbine elements, and process plant filters.

Materials in accordance with the invention made from microspheres of stabilized zirconium dioxide, 30—40 $m\mu$ in diameter, with a contact diameter of 0.3 of the microsphere diameter and a porosity of 30 volume per cent have been found to exhibit a compression strength of 6000 kg/cm², a tensile strength of 500 kg/cm², and 0.01 elongation at room temperature, which means a 5—10-fold increase compared with the corresponding characteristics of hitherto proposed granular materials of similar composition.

Materials made from aluminium oxide microspheres, 30—40 $m\mu$ in diameter with an intersphere contact diameter of 12—15 $m\mu$

and 35% porosity, showed a compression strength of 9000 kg/cm², a tensile strength of 950 kg/cm², and a relative deformation of 0.007, which is better than the corresponding characteristics of hitherto proposed porous materials by 7—10 times. Recrystallization velocity, which is expressed by alteration of grain (microsphere) geometry and size, is considerably lower than that of hitherto proposed materials. Thus, no secondary recrystallization was found in a material made from sintered aluminium oxide microspheres, 60—70 $m\mu$ in diameter, after being kept for 50 hours at a temperature of 1860°C.

Materials in accordance with the invention can contain a filler, provided the material is still porous. These filler materials can be employed for ablation thermal protection purposes, as a heat-resistant lining, or as an arc electrode. In this case, the fillers can be a metal, such as bismuth, copper or silver; a alloy, such as iron - nickel or chromium - iron - nickel alloys; or an intermetallic compound based on silver and aluminium with an aluminium content of 7.69 atomic per cent and a melting point of 779°C, an iron - nickel - based intermetallic compound with a nickel content of 75.9 atomic per cent or an aluminium - nickel - based intermetallic compound comprising 57.97 atomic per cent of aluminium.

The filler can also be an organic compound such as a phenol - formaldehyde resin, polyvinyl alcohol or an organosilicone polymer, e.g. a polyorganosiloxane, a siloxane thermosetting polymer, or a siliconalkyl polycondensate, or glass.

Fillers, when present, have the following effect:—

A heat-resistant material made from microspheres of zirconium dioxide stabilized by 6 weight per cent of calcium oxide, 92—100 $m\mu$ in diameter, and with a contact diameter between sintered microspheres of 30—40 $m\mu$ and a 35% porosity, had a compression strength of 800 kg/cm².

A material for the electrical engineering industry and having a similar composition and structure, but containing 30 volume per cent of bismuth, had a compression strength of 2100 kg/cm² and it was able to conduct an electric current at up to 100 A/cm² with a voltage of up to 50 V when operating under arc discharge conditions.

An ablation material, including 60 volume per cent of microspheres of zirconium dioxide stabilized by 15 weight per cent of yttrium oxide, 150 $m\mu$ in diameter with a contact diameter between the sintered microspheres of 40—45 $m\mu$, and in addition 35 volume per cent of an organosilicone polymer as a filler, was capable of operating without changes in geometry in contact with a com-

bustion product flow owing to evaporation of the polymer.

A heat-resistant thermostable material, made from 66 volume per cent of microspheres of zirconium dioxide stabilized by calcium oxide, 92—100 $m\mu$ in diameter with a contact diameter between said microspheres of 34—38 $m\mu$, additionally containing 25—30 volume per cent of glass with a thermal expansion coefficient of $1-3 \times 10^{-6}$ deg $^{-1}$, and shaped as a plate 17 mm thick, was capable of withstanding one-sided heating at a rate of 2—2.5 deg/s without cracking. This surpasses by 5—6 times the permissible heating rate of a plate that is similar in size but has been produced from hitherto proposed granular materials of similar composition and has an 18% porosity (the permissible heating rate for this material is from 0.2 to 0.3 deg/s).

Materials in accordance with the invention can be fabricated using known methods of ceramic technology dealing with non-plastic high-melting point oxides. Thus, separation of microspheres into fractions can be effected with the help of standard sieves or separators. Moulding of the materials can be accomplished:

1. by vibration in ceramic moulds;
2. by slip casting with subsequent drying; or
3. by semi-dry pressing also followed by drying.

A common final operation with all of these methods is sintering, preferably in a gas-fired open-flame furnace at a temperature of 0.8—0.9 of the melting point of the corresponding oxides with isothermal holding for 2—10 hours. Materials in accordance with the present invention which also include a filler can be manufactured by impregnation with appropriate substances and compounds. The impregnation methods may include:

- a) injection moulding;
- b) centrifugal casting;
- c) vacuum impregnation; or
- d) impregnation under the effect of capillary forces.

The following Examples are given by way of illustration only:—

Example 1

A heat-resistant porous material, made from microspheres of zirconium oxide stabilized by 6 weight per cent of calcium oxide, 50—65 $m\mu$ in diameter with a contact diameter between the sintered microspheres of 18—20 $m\mu$ and a porosity of 34 volume per cent had a compression strength of 2000 kg/cm 2 , a tensile strength of 250 kg/cm 2 , and an elongation of 0.8% at a temperature of 20°C. The microspheres of which the material

was composed were produced by plasma treating a powdered, stabilized, zirconium oxide.

The material fabrication process involved the following operations:

1. Separation of the microspheres in fractions with the help of a standard set of reciprocating sieves to obtain a fraction 50—56 $m\mu$ in diameter.

2. Vibration moulding (vibration placement) of the microspheres in a ceramic container of stabilized zirconium oxide. Spontaneous sintering in an oxygen-gas-fired furnace for 5 hours at a temperature of 2100°C.

Upon sintering, the container was separated from the material by machining.

Example 2

A material, as per Example 1 and additionally containing 26 volume per cent of a phenol - formaldehyde resin, was produced by impregnation with the resin in a vacuum chamber with subsequent polymerization of the resin. Following destruction and removal of the resin by heating, the material had the durability of a heat-insulating element without changing its geometry, with the resin being removed at a rate of 25×10^{-4} g/cm 2 .s.

Example 3

A material, as per Example 1 and additionally containing 20 volume per cent of polyvinyl alcohol, was manufactured by impregnation with polyvinyl alcohol in a vacuum chamber. Following destruction and removal of the resin in the material, a durable heat-insulating element was obtained without any changes in its geometry with the alcohol being removed at a rate of $5 \cdot 10^{-3}$ g/cm 2 .s.

Example 4

A material, as per Example 1 and additionally containing 30 volume per cent of bismuth, was manufactured by forced impregnation with bismuth in a chamber under a pressure of 50 atm. and at a temperature of 1000°C. The material was durable as an arc electrode at a current density of 80 A/cm 2 , without any changes in its geometry for 60 s.

Example 5

A heat-resistant porous material was produced according to Example 1 from 66 volume per cent of microspheres of zirconium dioxide stabilized by calcium oxide, 92—100 $m\mu$ in diameter with a contact diameter of the microspheres varying from 34 to 38 $m\mu$, and 25—30 volume per cent of glass with a thermal expansion coefficient of $1-3 \times 10^{-6}$ deg $^{-1}$, in the form of plates 17 mm thick, the plates withstood one-sided heating at a rate of 2—2.5 deg/s without cracking. This was 5—6 times the permissible heating rate for a plate of a similar size produced from a hitherto

proposed granular material of similar composition and an 18% porosity.

Example 6

A heat-resistant porous material as in Example 1 was impregnated in air at a temperature of 1020°C with an alloy consisting of silver and 1—2 weight per cent of copper oxide. Impregnation was carried out by capillary forces. The material shaped as a bar measuring 10×10×40 mm, or as a disk 30 mm in diameter and 10 mm thick, and containing 25—30 volume per cent of the alloy, did not crack when heated on one side in a gas flow to a temperature of 2200°C, and then cooled to room temperature at a rate of 2000°C deg/s. The material was capable of conducting an electric current having a density of up to 20 A/cm².

Example 7

A heat-resistant ablation material was made from 60 volume per cent of microspheres of zirconium dioxide stabilized by 15 weight per cent of yttrium oxide, 140—160 mμ in diameter with a contact diameter of the sintered microspheres varying from 40 to 45 mμ, and 35 volume per cent of an organosilicone polymer as a filler, the material was capable of operating without changes in geometry when brought into contact with a flow of combustion products, owing to destruction, and evaporation of the polymer. Impregnation with the polymer was carried out in a vacuum chamber under a pressure of 10⁻¹ mm Hg at a temperature of 100°C, followed by polymerization.

Example 8

A heat-resistant porous material was made from 65 volume per cent of microspheres of aluminium oxide, 30—40 mμ in diameter, with a contact diameter of the sintered microspheres being 12—15 mμ, the material had a compression strength of 9000 kg/cm², a tensile strength of 950 kg/cm², and an elongation of 0.7%. The microspheres from which the material was composed were produced by plasma processing powdered artificial corundum (Electrolytically produced corundum). The material was moulded by vibration of the microspheres in corundum crucibles. Sintering was effected in an oxygen-gas-fired furnace at a temperature of 1850°C, with isothermal holding for 5 hours.

Example 9

A material was obtained as in Example 8 from 65 volume per cent of microspheres of aluminium oxide, 60—70 mμ in diameter,

sintered directly to each other so that contact between the microspheres was 20—25 mμ. The material was not subject to secondary recrystallization during isothermal heat treatment for 50 hours at a temperature of 1800°C.

Example 10

A heat-resistant porous material was made from 65 volume per cent of microspheres of yttrium oxide, 30—40 mμ in diameter with a contact diameter between the sintered microspheres of 12—15 mμ. The material had a compression strength of 1850 kg/cm², a tensile strength of 200 kg/cm², and an elongation of 0.5%. The microspheres from which the material was composed were produced by plasma processing of powdered yttrium oxide. Sintering was effected in crucibles of stabilized zirconium dioxide in an oxygen-gas-fired furnace at a temperature of 2100°C with isothermal holding for 7 hours.

WHAT WE CLAIM IS:—

1. A heat-resistant porous material, comprising 50—75 volume per cent of microspheres of a high-melting point oxide having a melting point in excess of 1700°C, the microspheres being 10—200 mμ in diameter and being sintered directly to each other so that the diameter of the circle of contact between the microspheres is 0.2—0.5 of the microsphere diameter.

2. A heat-resistant porous material as claimed in claim 1, which additionally incorporates a filler which partly fills the pores of the material.

3. A heat-resistant porous material as claimed in claim 2, wherein the filler is a metal, an alloy, or an intermetallic compound.

4. A heat-resistant porous material as claimed in claim 2, wherein the filler is a phenol - formaldehyde resin, a polyvinyl alcohol, an epoxy resin, or an organosilicone polymer.

5. A heat-resistant porous material as claimed in claim 2, wherein the filler is glass.

6. A heat-resistant porous material as claimed in any of the preceding claims, substantially as hereinbefore described with reference to any of the Examples.

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